

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 January 2002 (31.01.2002)

PCT

(10) International Publication Number  
**WO 02/08514 A2**

(51) International Patent Classification<sup>7</sup>: **D21H**

(21) International Application Number: **PCT/US01/21809**

(22) International Filing Date: **9 July 2001 (09.07.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
**09/626,160** **26 July 2000 (26.07.2000)** **US**

(71) Applicant: **HERCULES INCORPORATED [US/US];**  
Hercules Plaza, 1313 N. Market Street, Wilmington, DE  
19894-0001 (US).

(72) Inventors: **NEWPORT, John, F., L.,;** 239 Pond View  
Drive, Chadds Ford, PA 19317 (US). **WEATHERDON,**  
**Jennifer;** 25 Hawthorne Avenue, Newark, DE 19711  
(US).

(74) Agent: **ROSSI, Joanne, Mary, Fobare;** Hercules Incor-  
porated, Hercules Plaza, 1313 N. Market Street, Wilming-  
ton, DE 19894-0001 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— *without international search report and to be republished  
upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: **METHOD OF MAKING SIZING EMULSION AND SIZING EMULSION**

(57) Abstract: The present invention relates to methods for preparing emulsions comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming an emulsion between the water and an oil phase comprising the sizing agent, and to emulsions comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming an emulsion between the water and an oil phase comprising the sizing agent.

**WO 02/08514 A2**

## METHOD OF MAKING SIZING EMULSION AND SIZING EMULSION

### 1. Field of the Invention

5 This invention relates to methods for making sizing emulsions and to sizing emulsions. The invention also relates to methods for using the sizing emulsions in papermaking.

### 2. Discussion of Background Information

10 An important property of paper, paperboard and similar products is resistance to penetration by water and other liquids. Two main methods for conferring resistance to water penetration are internal sizing and surface sizing. Internal sizing confers such resistance in the entire paper structure while the effect of surface sizing can be more or less limited to the virtual surface structure.

15 During the last few years, papermaking has changed. More and more water is recycled and some mills preferably run with closed water systems. A consequence has been a temperature increase throughout the stock and furnish wet-part preparation stages and wet end cycle of papermaking, to 70°C or greater in some mills. Frequently, this has been coupled with an increase in the pH throughout the same cycle, from, for example, pH 4-5 to pH 6-8, because, among other things, of the change from clays to carbonates as components of filled paper furnishes. Under these conditions, sizes lose efficiency due to saponification (for example, rosin saponification) and hydrolysis (for example, hydrolysis of cellulose reactive size, including  
20 ketene dimers or multimers, such as alkyl ketene dimers and alkenyl ketene dimers, and multimers thereof).

25 In addition to temperature and pH factors, other aspects of some paper machines can adversely create and exaggerate conditions for unfavorable chemistry. For example, some machines lack a degree of flexibility for experimentation with consequential or concurrent additions of sizing materials, alum and other wet part paper ingredients, in order to achieve efficiency gains. The dwell time of the papermaking chemicals with the fiber, from the points of addition, to the paper machine flow box, wire and press section exposes the chemicals to a hostile environment, which the compositions and processes of this invention serve to minimize.

30 Conventional sizing emulsions may comprise sizing agent, surfactant, starch, alum, and optionally polyaluminum chloride. If the sizing agent comprises ketene dimers, many of the

aforesaid problems have been obviated.

U.S. Patent No. 5,433,776 concerns a sizing composition comprising a stable aquasol of positively charged colloidal silica, positively charged colloidal alumina, or positively charged colloidal zirconia containing a ketene dimer size and a ketene dimer emulsifier, such as sodium lignin sulfonate. The composition may also contain stabilizers, such as cationic starch and cationic polymers, and other adjuncts in conjunction with the ketene dimer size emulsion.

U.S. Patent No. 5,876,562 concerns aqueous sizing dispersions comprising cellulose-reactive sizing agents, such as alkyl ketene dimer, and colloidal anionic aluminum-modified silica particles which dispersions have improved stability as compared to anionic sizing dispersions containing colloidal silica particles. The dispersions can contain from about 0.1 to about 30 percent by weight of cellulose-reactive sizing agent and the weight ratio of cellulose-reactive sizing agent to aluminum-modified silica can be within the range of from 1:1 to 100:1.

U.S. Patent No. 5,969,011 concerns an aqueous dispersion of a sizing agent containing a cellulose-reactive sizing agent, such as alkyl ketene dimer, and a dispersant system comprising a low weight cationic organic compound having a molecular weight of less than 10,000 and an anionic stabilizer which is an anionic polyelectrolyte. The patent teaches that the compounds of the dispersant system are bound together by the force of electrostatic attraction, thereby representing a coacervate dispersant. The anionic polyelectrolyte component may include microparticulate material.

U.S. Patent No. 5,627,224 concerns an aqueous sizing composition comprising alkyl ketene dimer and from 1 to 35% by weight based on the alkyl ketene dimer of stabilizing and/or dispersing agent, selected from amphoteric starches and amphoteric acrylamide based polymers, and from 0.1 to 10% by weight based on the alkyl ketene dimer of polyaluminum compound.

U.S. Patent No. 5,270,076 concerns a process for coating ketene dimer on titanium dioxide. U.S. Patent No. 5,145,522 concerns a stabilized ketene dimer sizing agent for papermaking consisting essentially of a dispersion of a ketene dimer in an aqueous phase containing dispersing agent and a polymeric aluminum compound selected from the group consisting of polymeric aluminum hydroxide, polymeric aluminum chloride and mixtures thereof. The dispersing agent can be a cationic dispersing agent, or a nonionic or anionic surface active agents. Cationic dispersing agents include cationic starch containing at least one kind of

primary, secondary and tertiary amino groups and quaternary ammonium salts or other cationic dispersing agents such as polyethyleneimine, polyethyleneimineepichlorohydrine condensate polyamidopolyamineepichlorohydrine resin, polyvinylpyridine, styrenedimethylaminoethyl acrylate copolymer, cationic polyurethane resin, dicyandiamide formaldehyde resin, urea formaldehyde resin, melamine formaldehyde resin, dimethylamine epichlorohydrine resin and the like. Nonionic dispersing agents can be polyvinyl alcohol or oxidized starch. However, if the amount of the polymeric aluminum hydroxide exceeds 10% by weight, the sizing effect is lowered.

U.S. Patent No. 2,865,743 concerns ketene coated on silica to form a free flowing powder.

### SUMMARY OF THE INVENTION

It has been unexpectedly discovered that a sizing agent, such as ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides and the like, can be emulsified in water with an inorganic particulate emulsifying agent capable of forming an emulsion of water and the sizing agent wherein the emulsifying agent comprises inorganic particulate capable of forming the emulsion.

Further, the invention relates to an emulsion comprising water, sizing agent and inorganic particulate emulsifying agent. The inorganic particulate emulsifying agent can be an inorganic particulate capable of forming an interface between water and an oil phase comprising the sizing agent.

Further, the invention relates to forming an emulsion comprising water, sizing agent and an inorganic particulate emulsifying agent in a batch operation, i.e., at a site other than the papermaking plant, wherein the inorganic particulate emulsifying agent comprises inorganic particulate capable of forming the emulsion.

Further, the invention relates to a method for continuously forming an aqueous emulsion comprising water, sizing agent, and inorganic particulate emulsifying agent capable of forming the emulsion of water and the sizing agent comprising adding the inorganic particulate emulsifying agent to an aqueous feed stream, adding the sizing agent to the feedstream comprising the inorganic particulate emulsifying agent to form the emulsion and feeding the stream comprising the emulsion into the headbox where the emulsion is mixed

with the pulp in the furnish at the site of the papermaking facility. The sizing agent may include, and is not limited to, sizing agents such as ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides, and the like. The emulsifying agent comprises inorganic particulate capable of forming the emulsion between water and an oil phase containing the sizing agent.

Also the present invention relates to a method for preparing an emulsion comprising water, sizing agent such as ketene dimer, alkenyl succinic acid anhydride, rosin, carbamoyl chloride and the like, and inorganic particulate emulsifying agent. The inorganic particulate emulsifying agent is an inorganic particulate capable of forming the emulsion of water and an oil phase containing the sizing agent.

The present invention relates to an emulsion comprising water, sizing agent such as ketene dimer, alkenyl succinic acid anhydride, rosin, carbamoyl chloride and the like, and an inorganic particulate emulsifying agent. The inorganic particulate emulsifying agent is an inorganic particulate capable of forming the emulsion of water and an oil phase containing the sizing agent. The emulsion may be used for internal sizing and/or surface sizing.

In a preferred aspect of the present invention, the emulsion comprises ketene dimer and an inorganic particulate emulsifying agent capable of forming the emulsion of water and an oil phase containing the ketene dimer. The inorganic particulate emulsifying agent comprises inorganic particulate capable of forming the emulsion and the emulsion is be used for internal sizing and/or surface sizing.

In another preferred aspect of the present invention, the emulsion comprises alkenyl succinic acid anhydride and an inorganic particulate emulsifying agent capable of forming the emulsion of water and an oil phase containing the ketene dimer. The inorganic particulate emulsifying agent comprises inorganic particulate capable of forming the emulsion and the emulsion is to be used for internal sizing and/or surface sizing.

The invention relates to a method of preparing an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the sizing agent, wherein the method comprises admixing water, the inorganic particulate emulsifying agent and the sizing agent to form the aqueous emulsion.

The invention relates to an aqueous emulsion comprising water, sizing agent and

inorganic particulate emulsifying agent capable of forming the emulsion between the water and the sizing agent.

5 In the aqueous emulsion and the method of preparing the aqueous emulsion, the inorganic particulate emulsifying agent may be selected from clay, silica, zeolite, mica, calcium carbonate, calcium phosphate, calcium sulfate, aluminum oxide, aluminum hydroxide, aluminum phosphate, aluminum silicate, magnesium phosphate, magnesium silicate, polyaluminum chloride, polyaluminum phosphate, polyaluminum silicate, ferrous phosphate, ferrous silicate, ferrous oxide, ferric phosphate, ferric silicate, ferric oxide, yttria, zirconia or mixtures thereof.

10 In the aqueous emulsion and the method of preparing the aqueous emulsion, the inorganic particulate emulsifying agent may also be selected from at least substantially water insoluble compounds of metals selected from aluminum, barium, calcium, cerium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, strontium, titanium, zinc, zirconium, or mixtures thereof or may be selected from colloidal silica, colloidal alumina or colloidal zirconia.

15 In the aqueous emulsion and the method of preparing the aqueous emulsion, the aqueous emulsion may comprise globules of the sizing agent emulsified with the inorganic particulate emulsifying agent and having a particle size of about 0.1 to about 100 microns, preferably having a particle size of about 0.1 to about 20 microns, and more preferably having a particle size of about 0.1 to about 2 microns.

20 In another embodiment of the present invention, the inorganic particulate emulsifying agent may be formed by dissolving a first water soluble salt in the water to form a solution comprising the first water soluble salt and adding a second water soluble salt to the solution to form the inorganic particulate emulsifying agent.

25 In a preferred embodiment of the present invention, the inorganic particulate emulsifying agent comprises polyaluminum particulate. The polyaluminum particulate may be formed by dissolving polyaluminum chloride in water to form a solution comprising the polyaluminum chloride and adding alkali to the solution to form the inorganic particulate emulsifying agent comprising polyaluminum particulate. The sizing agent may be selected from 2-oxetanone dimer or multimer, alkenyl succinic anhydride, rosin or carbamoyl chloride. The emulsion may be formed by admixing water, the sizing agent and the polyaluminum particulate to form a mixture  
30 and further sonicating or homogenizing the mixture of water, the sizing agent and the inorganic

particulate emulsifying agent to form the emulsion. The pH of the aqueous emulsion may be from about 4.3 to about 4.5.

It is especially preferred that the sizing agent comprises 2-oxetanone,3(C12-C16)alkyl,4-(C13-C17)alkylidene and the inorganic particulate emulsifying agent is polyaluminum particulate.

5           In another embodiment of the present method, the inorganic particulate emulsifying agent may be present in an amount from about 0.1 to about 100 percent by weight, based on the weight of the sizing agent and preferably in an amount from about 10 to about 25 percent by weight, based on the weight of the sizing agent.

10           In another embodiment of the present invention, where the sizing agent is solid at room temperature, the sizing agent may be heated to melt the sizing agent, the water may be heated to a temperature to at least about a melting point of the sizing agent, and the melted sizing agent, the heated water and the inorganic particulate emulsifying agent may be admixed to form the aqueous emulsion. In another aspect of the present invention where the sizing agent is solid at room temperature, the water may be heated to a temperature sufficient to melt the sizing agent.

15           In still another embodiment of the present invention wherein the sizing agent is solid at room temperature, the sizing agent may be dissolved in an organic solvent, and the water, the sizing agent dissolved in the organic solvent and the inorganic particulate emulsifying agent may be admixed to form the aqueous emulsion. Thereafter, the organic solvent is stripped from the emulsion.

20           In another preferred embodiment of the present invention, the sizing agent may comprise carbamoyl chloride and the inorganic particulate emulsifying agent may comprise polyaluminum particulate.

          In another preferred embodiment of the present invention, the sizing agent may comprise rosin and the inorganic particulate emulsifying agent may comprise polyaluminum particulate.

25           In a most preferred embodiment of the present invention, the sizing agent may comprise 2-oxetanone dimer or multimer and the inorganic particulate emulsifying agent may comprise polyaluminum particulate

30           The present invention also relates to adding the aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent to a pulp slurry in a headbox of a papermaking machine.

The present invention also relates to surface sizing paper with the aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent.

In another embodiment of the present invention, the present invention concerns a method for preparing an aqueous emulsion comprising water, wherein the sizing agent may comprise alkenyl succinic anhydride and wherein the inorganic particulate emulsifying agent may comprise polyaluminum particulate. The present invention also relates to adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine. The present invention also relates to surface sizing paper with the aqueous emulsion.

An especially preferred embodiment of the present invention relates to a method of preparing an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent comprising polyaluminum particulate, wherein the sizing agent is selected from one or more of 2-oxetanone,3-(C12-C16)alkyl,4-(C13-C17)alkylidene, 2-oxetanone,3-(C14-C16)alkyl,4-(C15-C17)alkylidene or 2-oxetanone,3-eicosyl,4-heneicosylidene, the method comprising: dissolving polyaluminum salt selected from one or more of polyaluminum chloride, polyaluminum hydroxychloride or polyaluminum chloride containing sulfate in water to form a solution, adding to the solution an amount of alkali sufficient to form a polyaluminum particulate, heating the water up to a melting temperature of the sizing agent, admixing the sizing agent with the heated water containing the polyaluminum particulate, and sonicating or homogenizing the admixed water to form the aqueous emulsion. In this embodiment of the invention, the sizing agent may be melted prior to its addition to the water. The invention also relates to adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine or surface sizing paper with the aqueous emulsion.

The present invention also relates to a method of preparing an aqueous emulsion comprising water, alkenyl succinic anhydride and inorganic particulate emulsifying agent comprising polyaluminum particulate, wherein the method comprises: dissolving polyaluminum salt selected from one or more of polyaluminum chloride, polyaluminum hydroxychloride or polyaluminum chloride containing sulfate in water to form a solution, adding to the solution an amount of alkali sufficient to form a polyaluminum particulate, admixing the alkenyl succinic anhydride with the water containing the polyaluminum particulate, and sonicating or homogenizing the admixed water to form the aqueous emulsion. The invention also relates to



adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine or surface sizing a paper with the aqueous emulsion.

The present invention also relates to an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the sizing agent wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

The present invention also relates to an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the sizing agent wherein the sizing agent is selected from carbamoyl chloride, rosin, 2-oxetanone dimer or multimer, or alkenyl succinic anhydride. In this embodiment of the present invention, the inorganic particulate emulsifying agent may comprise polyaluminum particulate; the sizing agent may be 2-oxetanone,3(C12-C16)alkyl,4-(C13-C17)alkylidene; and the pH of the aqueous emulsion ranges from about 4.3 to about 4.5. The inorganic particulate emulsifying agent may be present in an amount from about 5 to about 35 percent by weight, based on the weight of the sizing agent and preferably in an amount from about 10 to about 25 percent by weight, based on the weight of the sizing agent.

The present invention also relates to an aqueous emulsion wherein the sizing agent is carbamoyl chloride and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

The present invention also relates to an aqueous emulsion wherein the sizing agent is rosin and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

A preferred embodiment of the present invention relates to an aqueous emulsion wherein the sizing agent is 2-oxetanone dimer or multimer and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate. Another preferred embodiment of the present invention relates to an aqueous emulsion wherein the sizing agent is alkenyl succinic anhydride and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

The present invention also relates to a method of processing cellulosic pulp comprising adding to the cellulosic pulp, in a wet part of a papermaking process, an emulsion comprising

water, sizing agent and an inorganic particulate emulsifying agent.

The present invention also relates to a method of surface sizing paper with an emulsion comprising water, sizing agent and an inorganic particulate emulsifying agent.

5 The present invention also relates to an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the sizing agent and water, wherein the sizing agent is selected from one or more of 2-oxetanone,3-(C12-C16)alkyl,4-(C13-C17)alkylidene, 2-oxetanone,3-(C14-C16)alkyl,4-(C15-C17)alkylidene or 2-oxetanone,3-eicosyl,4-heneicosylidene, and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

10 An especially preferred embodiment of the present invention relates to a method of processing cellulosic pulp comprising adding to the cellulosic pulp, in a wet part of a papermaking process, the emulsion comprising water, a sizing agent selected from one or more of 2-oxetanone,3-(C12-C16)alkyl,4-(C13-C17)alkylidene,2-oxetanone,3-(C14-C16)alkyl,4-(C15-C17)alkylidene or 2-oxetanone,3-eicosyl,4-heneicosylidene, and polyaluminum particulate.

15 Another especially preferred embodiment relates to a method of surface sizing paper with the aforesaid emulsion.

The present invention also relates to an aqueous emulsion comprising water, alkenyl succinic anhydride and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the alkenyl succinic anhydride, wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

20 The present invention also relates to a method of processing cellulosic pulp comprising adding to the cellulosic pulp, in a wet part of a papermaking process, an emulsion comprising water, alkenyl succinic anhydride and polyaluminum particulate or surface sizing paper with the emulsion.

25 The present invention also relates to a paper product or cardboard made with an aqueous emulsion comprising water, sizing agent and an inorganic particulate emulsifying agent.

#### DETAILED DESCRIPTION OF THE INVENTION

30 The particulars shown herein are by way of example and for purposes of illustrative discussion of the various embodiments of the present invention only and are presented in the

cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

All percent measurements in this application, unless otherwise stated, are measured by weight of a component based upon 100% of the weight of the sizing agent.

Unless otherwise stated, a reference to a compound or component, includes the compound or component by itself, as well as in combination with other compounds or components, such as mixtures of compounds.

Paper is made by a process that includes forming a pulp or slurry, followed by forming the pulp or slurry into a membrane from which the paper sheet is eventually formed. The wet part (as this term is used herein) of the process includes all the stages in furnish preparation, including pulp blending and refining, through thick stock and thin stock blending, chemical additions and dilutions with both white water and fresh incoming water, to the point of deposition of fiber and membrane formation on the wire, at the wet end of the papermaking process. Thus, the wet part of the process includes all stages of the papermaking process through the formation of the sheet.

As used herein, internal sizing refers to sizing associated with the addition of sizing agent at the wet part of the papermaking process, and thus internal sizing or sizing at the wet part of the papermaking process refers to the addition of sizing agent at any of the stages of the wet part of the process.

As used herein, surface sizing is applied on the formed paper. Surface sizing may be carried out on the papermaking machine at a size press, which is a station between the dryer sections. Surface sizing may also be carried out on the papermaking machine in a tub sizing, where the paper sheet is run through a shallow bath comprising the sizing agent. The tub sizing may also be carried out in an off-machine operation.

The present invention relates to methods for preparing emulsions comprising water, sizing agent, and an inorganic particulate emulsifying agent capable of forming the emulsion of water and the sizing agent. The inorganic particulate emulsifying agent comprises inorganic particulate capable of forming the emulsion. The sizing agent may be, and is not limited to,

sizing agents such as ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides and the like. The term, "ketene dimers or multimers", is used to refer collectively to alkyl ketene dimers and alkenyl ketene dimers, and multimers of these materials.

The present invention also relates to emulsions comprising water, sizing agent, and an inorganic particulate emulsifying agent capable of forming the emulsion of water and the sizing agent. The inorganic particulate emulsifying agent comprises inorganic particulate capable of forming the emulsion. The sizing agent may be, and is not limited to, sizing agents such as ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides and the like.

Further, the invention relates to a method for continuously forming an aqueous emulsion comprising water, sizing agent, and inorganic particulate emulsifying agent capable of forming an emulsion with water and the sizing agent comprising adding the inorganic particulate emulsifying agent to an aqueous feed stream, adding the sizing agent to the feedstream comprising the inorganic particulate emulsifying agent, admixing the inorganic particulate emulsifying agent and the sizing agent to form the emulsion, and feeding the stream comprising the emulsion into the headbox where the emulsion is mixed with the pulp in the furnish at the site of the papermaking facility.

In one aspect of the present invention, the inorganic particulate emulsifying agent may comprise an inorganic particulate which is added to the aqueous feed stream.

In another aspect of the present invention, the inorganic particulate emulsifying agent may comprise a water soluble precursor which may be made into the inorganic particulate capable of forming the emulsion between water and an oil phase containing the sizing agent. Such a precursor may include, but is not limited to, water soluble inorganic compounds which by chemical reaction can form a water insoluble inorganic particulate capable of forming the emulsion. Thus, the inorganic particulate emulsifying agent may be made in situ and comprises an inorganic particulate. The skilled worker may not wish to convert all the water soluble precursor into inorganic particulate and may desire to keep a portion of the precursor as a water soluble salt, especially where the water soluble salt is useful, for example, for drainage and charge retention purposes. Depending upon the requirements of a papermaking process, the skilled worker can determine the amount of water soluble salt vis-a-vis insoluble inorganic

particulate that is needed. As a minimum, the amount of insoluble inorganic particulate should be sufficient to emulsify the oil phase comprising the sizing agent. It is also within the scope of the invention to have an amount of insoluble inorganic particulate greater than the amount necessary to emulsify the oil phase comprising the sizing agent, where the insoluble inorganic particulate may be used, for example, as a filler. Non-limiting examples are given below.

If the precursor is a solution of polyaluminum chloride, the skilled worker may convert with the addition of alkali to the solution the polyaluminum chloride into polyaluminum particulate. The skilled worker may choose to convert any amount of the polyaluminum chloride into polyaluminum particulate so long as the amount of the polyaluminum particulate is sufficient to emulsify all of a sizing agent to be added to the solution, the remaining polyaluminum chloride being useful, for example, as a drainage agent. It is also within the scope of the invention to have an amount of polyaluminum particulate which is more than the amount sufficient to emulsify the sizing agent, especially where the particulate will be useful, for example, as a filler for paper. Thus, the emulsion may comprise water, sizing agent, water soluble polyaluminum chloride, and polyaluminum particulate wherein the polyaluminum particulate is at least in an amount sufficient to form the emulsion between the water and the sizing agent.

If the precursor is a solution of alum, the skilled worker may add sodium silicate or phosphate to the solution to convert the alum into aluminum silicate or phosphate particulate. The skilled worker may choose to convert any amount of the alum into aluminum silicate or phosphate particulate so long as the amount of the aluminum silicate or phosphate particulate is sufficient to emulsify all of a sizing agent to be added to the solution, the remaining alum being useful, for example, for charge retention. Thus, the emulsion may comprise water, sizing agent, alum, and aluminum silicate or phosphate particulate, wherein the aluminum silicate or phosphate particulate is at least in an amount sufficient to form the emulsion between the water and the sizing agent.

If the precursor is a solution of ferric chloride, the skilled worker may add alkali, such as sodium hydroxide, to the solution to convert the ferric chloride to ferric hydroxide particulate.

The skilled worker may choose to convert any amount of the ferric chloride into ferric hydroxide particulate so long as the amount of the ferric hydroxide particulate is sufficient to

emulsify all of a sizing agent to be added to the solution.

Thus, the emulsion can be prepared on demand on site. If the sizing agent is ketene dimer, its drainage and sizing characteristics can be accessed regardless of stability. If the sizing agent is alkenyl succinic acid anhydride, it is possible to retard the hydrolysis of the alkenyl succinic acid anhydride in order to permit it to react with the pulp in the furnish. Many conditions, such as pH, temperature, concentration of emulsifying agent, viscosity, density difference between the aqueous and emulsified or dispersed phases, or the amount of the emulsified or dispersed phase, may affect the long term stability of an emulsion; however, since the emulsion is being made on site, the skilled worker need not be concerned with the long term stability of the emulsion, but rather is concerned with forming the emulsion and having it stable long enough to be processed for internal sizing in the wet part of the papermaking process or surface sizing at a subsequent stage in the papermaking process.

Because of the possible drainage characteristics of some of the ketene dimer emulsions of the present invention, when they are used at the wet part of the papermaking process, less energy is utilized to dry the wet formed paper product. Further, faster drainage allows the papermaking machines to be run faster.

Also the present invention relates to the preparation of alkenyl succinic acid anhydride emulsions with an inorganic particulate emulsifying agent capable of forming the emulsion of water and an oil phase comprising alkenyl succinic acid anhydride.

With the present invention, it is possible to modify the hydrolysis characteristics of an alkenyl succinic acid anhydride emulsion, i.e., to retard the hydrolysis of alkenyl succinic acid anhydride in order to permit it to react with the pulp in the furnish and to be used as a surface size.

In accordance with one aspect of the invention, the aqueous emulsions of the present invention which contain a sizing agent, such as ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides and the like, may be emulsified with an inorganic particulate emulsifying agent comprising an inorganic particulate emulsifying agent, which is capable of forming the emulsion with water and the sizing agent. These emulsions comprising sizing agents are useful for processes which utilize such agents.

In accordance with another aspect of the invention, the invention relates to methods of

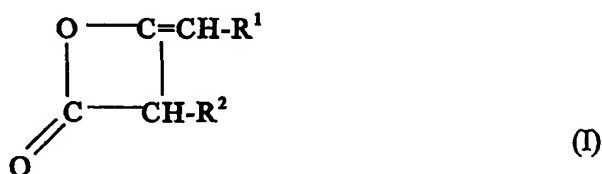
processing pulp with sizing agent, comprising adding to cellulosic pulp, in a wet part of a papermaking process, an emulsion comprising water, the sizing agent, and an inorganic particulate emulsifying agent which is capable of forming the emulsion between the water and an oil phase containing the sizing agent.

5 In accordance with another aspect of the invention, the invention relates to methods of surface sizing paper comprising sizing paper with an emulsion comprising water, sizing agent and an inorganic particulate emulsifying agent which is capable of forming the emulsion between the sizing agent and the water.

10 The present invention may utilize any sizing agent which is capable of being incorporated into an emulsion comprising water, sizing agent and inorganic particulate emulsifying agent which is capable of forming the emulsion between the sizing agent and the water. The sizing agents may include, but are not limited to ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides and the like, and mixtures thereof. The sizing agent may be liquid. If the sizing agent is solid, the sizing agent may be melted prior to the addition to the  
15 water that has been preheated to about the melting point of the solid sizing agent. On the other hand, the water may be heated to a sufficient temperature to melt the sizing agent prior to the addition of the sizing agent to the heated water.

#### Ketene Dimer and/or Multimer Compounds

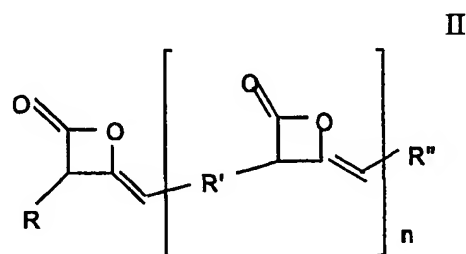
20 Ketene dimers and multimers suitable in this invention include ketene dimer and multimer materials selected from alkyl (straight or branched) ketene dimers, alkenyl (straight or branched) ketene dimers, multimers of alkyl ketene dimers and alkenyl ketene dimers, or mixtures of the foregoing. Preferred compounds include ketene dimers of formula I,



wherein  $R^1$  and  $R^2$ , which can be the same or different, are organic hydrophobic groups, preferably saturated or unsaturated hydrocarbon structures such as alkyl and alkenyl (each can independently be straight or branched chain) having at least 6 carbon atoms, more preferably at least 8 carbon atoms, cycloalkyl having at least 6 carbon atoms, aryl, aralkyl and alkaryl, and preferably straight or branched alkyl and alkenyl groups of 12 to 30 carbon atoms, more preferably 16 to 22 carbon atoms, and in some embodiments, most preferably 16-18 carbon atoms. Thus,  $R^1$  and  $R^2$ , which can be the same or different, can have mono or polyunsaturation, can be straight or branched chained, and have from about 1 to about 5 double bonds in the chain, preferably from about 1 to about 3 double bonds and more preferably 1 or 2 double bonds and contain the carbon atom ranges specified above.

Expanding on the above, in cases where  $R^1$  and  $R^2$  are both saturated, the compounds of formula I can be termed alkyl ketene dimers. However, in cases wherein one or both of  $R^1$  and  $R^2$  contain unsaturation (by virtue of, for example, the presence of one or more double bonds) the compounds of formula I can be termed alkenyl ketene dimers. Thus, both alkyl ketene dimers and alkenyl ketene dimers are embraced by the term ketene dimers herein, and therefore by formula I.

Suitable ketene multimers for use in the present invention include compounds of formula



(II)

wherein R and  $R''$  are the same or different and are an organic hydrophobic group having at least 6 carbon atoms, independently selected from straight (linear) or branched alkyl or straight (linear) or branched alkenyl;



R' is a branched or straight chain, or alicyclic, of from about 1 to about 40 carbon atoms;  
and n is an integer of from 1 to about 20.

The ketene dimers and multimers useful in the present invention can include compounds of formula I alone, compounds of formula II alone, or mixtures of compounds of formulae I and II.

Examples of suitable ketene dimers for use in the present invention are disclosed in U.S. Patent Nos. 4,522,686; 4,816,073; 4,927,496; and co-pending U.S. Patent Application No. 08/965,062, filed November 5, 1997, which are incorporated by reference for their disclosures of alkyl ketene dimers, alkenyl ketene dimers, and starting materials for making such ketene dimers.

Examples of suitable ketene multimers, e.g. 2-oxetanone-based ketene multimers, are also well-known to those of ordinary skill in the art and are disclosed in U.S. Patent No. 5,846,663, which is incorporated by reference. Referring to formula (II) above, suitable ketene multimers for use with the present invention are those wherein n is an integer of at least 1, preferably 1 to about 20 and more preferably about 1 to about 8, even more preferably about 1 to about 6, and even more preferably about 2 to about 5.

Mixtures of the 2-oxetanone ketene multimers preferably contain regio isomers of such multimer compounds and preferably contain an average n of from about 1 to about 6 and more preferably from about 2 to about 5. Such mixtures of 2-oxetanone ketene multimers may also contain some 2-oxetanone ketene dimer, *i.e.*, n=0 in formula (II) (of course, as will be readily understood, when n=0, a compound in accordance with formula (I) results), as a consequence of the preparation method (described below) used to make the multimers.

R and R" are substantially hydrophobic in nature, are acyclic, are preferably hydrocarbons of at least about 4 carbon atoms in length, preferably at least 6, and may be the same or different. R and R" are more preferably about 10 to about 20 carbons in length and most preferably about 14 to about 16 carbons in length.

R and R", which may be the same or different, are preferably independently selected from the group of straight (linear) or branched alkyl, or straight (linear) or branched alkenyl. R and R" are more preferably linear alkenyl. Preferably not all R and R" substituents are straight alkyl chains and preferably at least 25% by weight of the sizing agent comprises the 2-oxetanone

structure in which at least one of R and R" is not straight chain (linear) alkyl. R and R" are ordinarily derived from a monocarboxylic acid reactant, *e.g.*, fatty acid and preferably an unsaturated fatty acid, when the ketene multimer is prepared from reaction of a monoacid component with a diacid component.

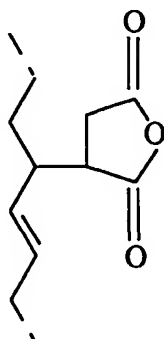
5           Examples of ketene dimers and multimers which can be employed in the present invention include the PRECIS® sizing agents commercially available from Hercules Incorporated, and which are disclosed in U.S. Patent No. 5,685,815, which is hereby incorporated by reference as though set forth in full herein. U.S. Patent No. 5,725,731, which is hereby incorporated by reference as though set forth in full herein, discloses ketene dimers and  
10           multimers useful in the invention that are made from saturated and unsaturated fatty acids and emulsions thereof. U.S. Patent No. 5,846,663, which is hereby incorporated by reference as though set forth in full herein, discloses ketene multimers useful in the invention. Canadian Patent 2,117,318, laid open December 11, 1994, which is hereby incorporated by reference as though set forth in full herein, discloses ketene multimers and emulsions thereof useful in the  
15           present invention.

          Examples of preferred commercial ketene dimers include PRECIS® 800 (for those compounds wherein R<sup>1</sup> and R<sup>2</sup> are primarily in the C16 range) (IUPAC name: 2-oxetanone,4-(8-heptadecenylidene),3-(7-hexadecenyl) CAS number 56000-16-9) (liquid at room temperature); AQUAPEL® 364 (for those compounds wherein R<sup>1</sup> and R<sup>2</sup> are primarily in the C16-18 range)  
20           (IUPAC name: 2-oxetanone,3-(C12-C16)alkyl,4-(C13-C17)alkylidene; CAS number 84989-41-3) (M.P. 40-47°C); AQUAPEL® 291 (for those compounds wherein R<sup>1</sup> and R<sup>2</sup> are primarily in the C18 range) (IUPAC name: 2-oxetanone,3-(C14-C16)alkyl,4-(C15-C17)alkylidene; CAS number 98246-81-8) (M.P. 60-62°C); and AQUAPEL® 532 (for those compounds wherein R<sup>1</sup> and R<sup>2</sup> are primarily in the C22 range) (IUPAC name: 2-oxetanone,3-eicosyl,4-heneicosylidene  
25           (CAS number 83707-14-9) (M.P. 63-64°C).

#### Alkenyl succinic acid anhydride

          Alkenyl succinic anhydrides in accordance with the present invention are preferably  
30           composed of unsaturated hydrocarbon chains containing pendant succinic anhydride groups. They are usually made in a two-step process starting with alpha olefin. The olefin is first

isomerized by randomly moving the double bond from the alpha position. In the second step the isomerized olefin is reacted with maleic anhydride to give the final alkenyl succinic acid anhydride having formula III:



(III)

Specific examples are isooctadecenyl succinic anhydride, n-octadecenyl succinic anhydride, n-hexadecenyl succinic anhydride, n-dodecyl succinic anhydride, i-dodecenyl succinic anhydride, n-decenyl succinic anhydride and n-octenyl succinic anhydride.

Examples of alkenyl succinic anhydrides useful in the present invention are disclosed in U.S. Patent No. 4,040,900, which is incorporated herein by reference in its entirety, and by C.E. Farley and R. B. Wasser in *The Sizing of Paper, Second Edition*, edited by W. F. Reynolds, Tappi Press, 1989, pages 51-62, which is incorporated by reference herein. A variety of alkenyl succinic anhydrides is commercially available from Bercen, Inc., a division of Cranston Print Works Company, Cranston, RI. or from Dixie Chemical Company, Inc., Houston, TX. Alkenyl succinic anhydrides for use in the invention are preferably liquid at 25°C. More preferably they are liquid at 20°C.

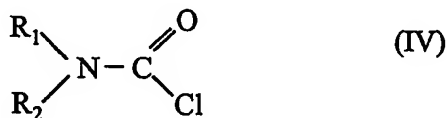
#### Rosin

Rosin materials, useful in the present invention, are well known to those of ordinary skill in the papermaking art. Examples of such rosin materials are discussed in U.S. Patent Nos.

4,743,303 and 4,522,686, which are incorporated by reference in their entireties. Such rosin, may include and is not limited to, tall oil rosin, wood rosin and gum rosin. The rosin may be fortified or adducted by reaction with an  $\alpha,\beta$ -unsaturated polybasic acid or anhydride. The rosin may also be modified by mixture with rosin esters or by direct esterification with for example glycerol or pentaerythritol. Rosin anhydrides, which are derivatives of rosin, may also be used in this invention.

#### Carbamoyl Chlorides

Examples of carbamoyl chlorides useful in the present invention are disclosed in U.S. Patent Nos. 4,743,303 and 3,966,484, whose disclosures are incorporated herein by reference in their entireties. Such carbamoyl chlorides include, and are not limited to, those having formula IV:



wherein  $R_1$  is an organic, hydrophobic group having about 8 to about 40 carbon atoms and  $R_2$  is H, lower alkyl, or an organic, hydrophobic group having about 8 to about 40 carbon atoms. Preferably,  $R_1$  and  $R_2$  may be organic hydrophobic groups, and more preferably alkyl groups having from about 12 to about 30 carbon atoms.

#### Inorganic Particulate Capable of Emulsifying Reactive Sizing Agent and Water

Any inorganic particulate, which is capable of acting as an emulsifying agent to form an emulsion between water and a sizing agent, such as ketene dimers or multimers, alkenyl succinic acid anhydrides, rosins, carbamoyl chlorides and the like, and mixtures thereof, may be used in the present invention. As used herein, inorganic particulate means that the particulate is inorganic and does not contain any organic material. However, the surface properties of the

inorganic particulate may be modified by physical adsorption or chemisorption to incorporate into the surface or portion thereof an organic material, such as a hydrophobic material. Preferably, the particulate is entirely inorganic and does not contain any organic material on its surface. While the inventors do not wish to be bound as to any theory as to why an inorganic particulate is useful as an emulsifying agent, it is believed that the inorganic particulate is capable of forming an interface between an oil phase comprising the sizing agent and water. The inorganic particulate is at least substantially insoluble in water and preferably insoluble in the oil phase comprising the sizing agent.

The inorganic particulate emulsifying agent may be cationic, anionic or nonionic. For example, polyaluminum particulate, which is formed by the neutralization of polyaluminum chloride with sodium hydroxide, is cationic.

#### 1. Substantially Insoluble Inorganic Particulate Emulsifying Agent

Any inorganic particulate, which is at least substantially insoluble in water, may be used so long as it is capable of forming an emulsion with water and sizing agent. Examples of inorganic particulate may include, but are not limited to, those materials selected from clay such as bentonite, exfoliated clay and the like; silica; zeolite; mica; calcium compounds, such as calcium carbonate, calcium phosphate, or calcium sulfate; magnesium compounds, such as magnesium phosphate, magnesium silicate, and the like; yttria; zirconia; aluminum compounds, such as aluminum oxide, aluminum hydroxide, aluminum phosphate, or aluminum silicate; polyaluminum compounds, such as polyaluminum chloride, polyaluminum phosphate or polyaluminum silicate; iron compounds, such as ferrous or ferric phosphate, silicate, or oxide and the like.

Also the inorganic particulate may include, but is not limited to, at least substantially water insoluble compounds of metals selected from aluminum, barium, calcium, cerium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, strontium, titanium, zinc, zirconium, or mixtures thereof.

The inorganic particulate emulsifying agent may have any three dimensional shape as long as it will form an emulsion with water and an oil phase comprising a sizing agent. While

the inventors do not wish to be bound to any theory, it is believed that the inorganic particulate will surround or coat globules of the oil phase comprising the sizing agent, thus emulsifying or dispersing the globules throughout the water. Such three dimensional shapes, include but are not limited to, spherical, oblong, ovoid, angular, granular, cylindrical, platelet, polyhedral, fibril, porous, floc, solid or hollow, and irregular.

## 2. Water Soluble Inorganic Compounds Useful for Making Substantially Insoluble Inorganic Particulate Emulsifying Agent

Water soluble inorganic compounds may also be used so long as they will form an inorganic particulate when admixed with an acid, a base or a salt.

For example, a water soluble inorganic salt and either acid or base, depending upon the nature of the inorganic salt, are admixed in order to form a particulate. Preferably, the water soluble salt is first dissolved in water and thereafter the acid or base is added in order to form the particulate. In some instances, the formed particulate may develop over a period of 24 hours or more a structure which appears to be gelled throughout the whole solution with little or no settling, i.e, when the particulate is first formed in water, the water containing the particulate has a low viscosity, but over a period of 24 hours or more, the viscosity increases due to the gelling. Thus, if the particulate has the tendency to develop a structure which appears to be gelled, it is preferable that the emulsion of sizing agent and inorganic particulate be made after the particulate is formed and before the particulate develops the gelled structure. The gelled structure may be thixotropic and can be broken apart by stirring or shearing. If the particulate develops a gelled structure, it may be utilized to form the emulsion of water, sizing agent and particulate.

The viscosity of the gelled particulate may range from 1 to 10,000 cps, preferably from 1 to 1,000 cps, most preferably from 1 to 500 cps. The viscosity of the gelled particulate may be adjusted by the amount of acid or base which is added to the aqueous medium. The viscosity is measured by a Brookfield Viscometer, Model LVF, (available from Brookfield Engineering Laboratories, Inc. Stroughton, MA) with spindle # 1 at 60 RPM at a temperature of 25° C. The pH is adjusted by variably adding standard acids or bases to raise or lower the pH as necessary dependent upon the composition of the particulate. Sulfuric acid, hydrochloric acid or the like

may be advantageously employed to lower pH and alkaline materials, e.g., sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium bicarbonate and the like, may be employed to increase pH.

Depending upon the nature of the water soluble salt, the skilled worker may raise or lower the pH of a solution containing the water soluble salt in order to form a particulate. The skilled worker may not wish to convert all of the water soluble salt to a particulate, because the water soluble salt may perform a useful function, such as charge retention control or drainage control whereas the particulate will serve as an inorganic particulate emulsifying agent. The skilled worker also will be aware that certain water soluble metal salts, such as polyaluminum chloride, alum or sodium aluminate, can be converted into particulate but if too much acid or alkali is used, the particulate can be redissolved. An example of this is described below.

For example, a solution comprising polyaluminum chloride is acidic and when alkali is added to the solution, a polyaluminum particulate starts to form at a pH of about 2. However, as more alkali is added to the solution, the pH is raised higher and the polyaluminum particulate will start to redissolve into the solution at a pH of about 4.8. It is preferred that sufficient alkali be added to the polyaluminum chloride solution in order to convert a desired amount of the polyaluminum chloride into polyaluminum particulate, the desired amount being the amount of polyaluminum particulate sufficient to emulsify all the sizing agent to be added to the emulsion, with the remaining polyaluminum chloride being useful for conferring drainage benefits.

Another method for forming a substantially water insoluble particulate is by double decomposition, also known as metathesis. Metathesis is a chemical reaction in which there is an exchange of elements or radicals according to the general equation:  $AB + CD = AD + BC$ . In accordance with the present invention, the compounds AB, CD and AD are soluble in water whereas BC is at least substantially insoluble in water, thereby forming a substantially water insoluble particulate. It is not critical whether all the water soluble salt is converted into substantially water insoluble particulate. For example, the remaining water soluble salt may be useful for drainage, charge retention or for some other purpose and for that reason, the skilled worker may not want to have a 100% conversion to the particulate.

Examples of such water soluble compounds, include but are not limited to, polyaluminum chlorides, alum, soluble salts of aluminum, iron, magnesium, manganese, calcium, chromium,

titanium, zirconium, nickel, cobalt, cerium, barium and the like.

Examples of metathesis type reactions are as follows:

Polyaluminum chloride when admixed with alkali, such as sodium hydroxide, will result in the formation of polyaluminum hydroxychloride particulate.

5 Alum when admixed with sodium silicate or phosphate will result in the formation of aluminum silicate or phosphate particulate.

Aluminum nitrate when admixed with sodium phosphate will result in the formation of aluminum phosphate particulate.

10 Ferric chloride when admixed with alkali, such as sodium hydroxide, will result in the formation of ferric hydroxide particulate.

Calcium chloride when admixed with sodium silicate or carbonate will result in the formation of calcium silicate or carbonate particulate.

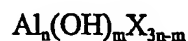
Barium acetate when admixed with sodium phosphate or sulfate will result in the formation of barium phosphate or sulfate particulate.

15 Zirconium tetrachloride or nitrate when admixed with sodium phosphate or silicate will result in the formation of zirconium phosphate or silicate particulate.

### 3. Polyaluminum Compounds Useful for Making Inorganic Particulate

20 Examples of polyaluminum compounds useful in this invention are those containing hydroxy groups and anions. Polyaluminum compounds such as polyaluminum chloride, polyaluminum hydroxychloride and polyaluminum chloride containing sulfate are in themselves well-known compounds and have been used in papermaking. Polyaluminum chlorides are also known as polyaluminum hydroxychloride and polyaluminum chlorohydroxide.

25 Examples of suitable polyaluminum compounds include those having the general formula



30 wherein X is a negative ion such as chloride or acetate and both n and m are positive integers so



that  $3n-m$  is greater than 0. Preferably X is Cl and such polyaluminum compounds are known as polyaluminum chlorides (PAC). Polyaluminum chlorides may also contain anions from sulfuric acid, phosphoric acid, polyphosphoric acid, chromic acid, dichromic acid, silicic acid, citric acid, carboxylic acids or sulfonic acids.

5           Examples of polyaluminum compounds useful in the present invention include, but are not limited to, those polyaluminum compounds disclosed in U.S. Patent Nos. 4,816,073; 5,192,363; 5,501,171; and 5,627,224; the disclosures of which are incorporated herein by reference.

10           Examples of preferred polyaluminum compounds in the present compositions are polyaluminum chlorides, which include Hyper<sup>+</sup> Ion® 1026 (available from General Chemical, Parsippany, NJ), Hyper<sup>+</sup> Ion® 1090 or Gen Pac 4370 (available from General Chemical), Hyper<sup>+</sup> Ion® 2021 (available from General Chemical), Gen<sup>+</sup> Ion® 7026 (available from General Chemical), Gen<sup>+</sup> Ion® 7033 (available from General Chemical), and Sumaclear 9108 (available from Summitt Research Labs, Huegenot, NY).

15           An inorganic particulate emulsifying agent comprising polyaluminum can be prepared by admixing an effective amount of basic solution, such as sodium hydroxide, potassium hydroxide, ammonium solution or the like, with polyaluminum chloride in solution to produce particulate in the solution, such that the particulate develops a structure which appears to be gelled throughout the whole solution with little or no settling over a period of 24 hours. It is  
20           preferred that about 20% of the polyaluminum chloride be converted to particulate, the remaining water soluble polyaluminum chloride being useful for drainage. The viscosity of the gelled particulate develops with time and takes about 24 hours to build up. The viscosity of the gelled particulate may range from 1 to 10,000 cps, preferably from 1 to 1,000 cps, most preferably from 1 to 500 cps. The pH of the aqueous medium containing the particulate may range from about  
25           2 to about 4.8. At a pH of about 2, the particulate will be formed and at a pH of about 4.8, the particulate will start to redissolve into solution. The pH is preferably from about 3 to about 4.8, and more preferably from about 4.3 to about 4.6.

30           The chemistry of the polyaluminate particulate is fairly complex and the inventors do not wish to be bound by any theory as to why the sizing agent is emulsified. It is believed that the stabilizing particulate is aluminum hydroxide, hydrated alumina or poly (aluminum hydroxy

chloride) species and that it is shaped in the form of platelets which surround the sizing agent globules.

In the case of polyaluminum chloride, the final pH of the solution with the particulate is, preferably, in the range from about 4.3 to about 4.5 and the particulate develops a structure which appears to be gelled throughout the whole solution with little or no settling on standing for 24 hours or more.

#### 4. Aquasols Useful as Inorganic Particulate Emulsifying Agents

The inorganic particulate emulsifying agent capable of forming an emulsion between an oil phase comprising sizing agent and water may be also include stable aquasols. Such stable aquasols comprise inorganic particulate in the form of colloidal silica, alumina, yttria, zirconia and oxides of iron. Typically, such sols start with colloidal, dense, finely divided particles, e.g., silica, generally having a surface area of about 20 to 600 square meters per gram, about 5 to about 150 nanometers in diameter, that are generally solubilized with a small amount of an alkali, such as sodium hydroxide. Exemplary sols are those containing positively charged particles having a dense silica core coated with a polyvalent metal-oxygen compound along with an anionic counter-ion. These and other sols are well known as disclosed in U.S. Patent Nos. 3,007,878; 3,620,978; 3,719,607; 3,745,126; 3,956,171; and 5,433,776; the disclosures of which are incorporated herein by reference. Examples of stable aquasols of colloidal silica include Ludox®CL and Ludox® HS-40 available from the DuPont Specialty Chemicals, Wilmington, Del. Examples of stable aquasols of colloidal zirconia include zirconia-nitrate stabilized available under the name NYACOL® Zr-50-20 from Nyacol Products Inc., Ashland, Mass. Examples of stable aquasols of colloidal alumina include a colloidal alumina dispersion available under the name NYACOL® Al-20 from Nyacol Products Inc.

#### Preparation of Emulsions Comprising Sizing Agent and Inorganic Particulate Emulsifying Agent

The aqueous medium comprising the inorganic particulate is used to prepare an emulsion comprising water and an oil phase comprising sizing agent wherein the oil phase is dispersed or

emulsified in the water.

While the inventors do not wish to be bound as to any theory as to the characteristics of the emulsified sizing agent, it is believed that the oil phase comprises the emulsified sizing agent in the form of droplets or globules coated with the inorganic particulate. The globules may have a mean particle size ranging from about 0.1 microns to about 100 microns, preferably from about 0.1 micron to about 50 microns, more preferably from about 0.1 micron to about 20 microns, and most preferably from about 0.1 micron to about 2 microns. A mean particle size of from about 0.2 micron to about 1 micron is especially preferred. The mean particle size may be determined by optical light scattering techniques with a Malvern Micro Plus Particle Size Analyzer, available from Malvern Instruments Inc., Southborough, MA.

To make the emulsion, a liquid-sizing agent, such as a ketene dimer or multimer, an alkenyl succinic acid anhydride, rosin, carbamoyl chloride and the like, is added to an aqueous medium comprising an inorganic particulate capable of emulsifying the sizing agent and water and is mixed sufficiently to form the emulsion.

The inventors do not wish to be limited to any particular technique for mixing the sizing agent and the aqueous medium comprising an inorganic particulate capable of emulsifying the sizing agent and water to form an emulsion comprising water, the sizing agent and the inorganic particulate. Rather, the inventors intend that any mixing technique known in the art may be utilized so long as the mixing will result in the formation of the emulsion. Preferably, the mixing may comprise homogenizing or sonicating.

The sizing agent may be liquid at room temperature and may be added to the aqueous medium containing the inorganic particulate. Thereafter, the aqueous medium comprising the sizing agent and the inorganic particulate is mixed sufficiently to form an emulsion comprising the sizing agent and the inorganic particulate. The mixing may comprise homogenization or sonification to form the emulsion.

If the sizing agent is solid at room temperature, the sizing agent may be melted and then added to the preheated aqueous medium comprising the inorganic particulate, the aqueous medium being heated to a temperature at least about the melting point of the solid sizing agent. Thereafter, the aqueous medium comprising the sizing agent and the inorganic particulate is mixed sufficiently to form the emulsion. Preferably, the mixing may comprise homogenizing

or sonicating to form the emulsion.

It is within the scope of the invention if the sizing agent is solid at room temperature to dissolve the solid sizing agent in a suitable organic solvent to form a solution containing the sizing agent. The solution containing the sizing agent may be added to the aqueous medium to  
5 allow the emulsion to be formed preferably at room temperature. Subsequently, the organic solvent can then be stripped from the emulsion by the application of heat and/or vacuum, as described in U.S. Patent Nos. 5,846,308 and 3,565,755, the disclosures of which are expressly incorporated by reference herein in their entireties.

It is also within the scope of the present invention if the sizing agent is solid at room  
10 temperature to add the solid sizing agent to the aqueous medium comprising the inorganic particulate, provided that the aqueous medium is heated to a temperature sufficient to melt the sizing agent. Thereafter, the aqueous medium comprising the inorganic particulate and the sizing agent is mixed sufficiently to form an emulsion. Preferably, the mixing step may comprise homogenizing or sonicating the emulsion.

15 The weight ranges of sizing agents and inorganic particulate emulsifying agent can be as follows:

The inorganic particulate emulsifying agent may range from about 0.1 to about 100 parts by weight or more, based upon 100 parts by weight of sizing agent. For purposes of cost, the amount of the particulate should be at least that amount sufficient to form the emulsion with  
20 water and the sizing agent. If the particulate or its precursors perform some other useful function for the papermaker, the papermaker may use more of the particulate and/or its precursors than the amount of particulate which is sufficient to form the emulsion.

In a preferred embodiment of the present invention, polyaluminum chloride is used to form a polyaluminum particulate. Polyaluminum chloride is dissolved in water and a base, such  
25 as sodium hydroxide, is added, thereby resulting in the formation of a polyaluminum particulate in the water. It is most preferred that about 20% of the polyaluminum chloride be converted to particulate. An emulsion is formed by sufficiently admixing sizing agent, such as ketene dimer or multimer, and the water containing the particulate. The emulsion may have a pH ranging from about 2 to about 4.8, preferably from about 3 to about 4.8 and more preferably from about 4.3  
30 to about 4.5. The pH of the emulsion can affect stability. If the emulsion is manufactured and

is to be used at a papermaking facility, the emulsion should be stable for at least 3 months, i.e., from the date of manufacture through storage and date of use. For the emulsion to be stable for this period of time, the emulsion should preferably have a pH ranging from about 4.3 to about 4.5.

5           On the other hand, if an emulsion comprising water, ketene dimers and/or multimers and an inorganic particulate emulsifying agent comprising polyaluminum particulate is formed at a papermaking plant and is incorporated as a stream in papermaking, the pH may range from about 2 to about 4.8. The lower limit of about 2 is the pH at which the particulate will start to form upon the addition of sodium hydroxide to the solution comprising polyaluminum chloride. The  
10           upper limit of about 4.8 is the pH at which the particulate will start to redissolve into the water.

          As noted previously, certain water soluble salts, such as polyaluminum chloride, alum or sodium aluminate, can be converted into particulate by the addition of acid or alkali, but if too much acid or alkali is added, the particulate can be redissolved. However, in most cases a particulate formed from a water soluble salt cannot be redissolved in water regardless of pH.  
15           Likewise, the pH range over which the stability of an emulsion formed with any particulate may vary widely and the pH range may be determined by one skilled in the art.

          The skilled worker may adjust the pH of an emulsion by variably adding acids or bases to raise or lower the pH. Acids, such as sulfuric acid, hydrochloric acid and the like, may be advantageously employed to lower pH and alkaline materials, such as caustic soda, sodium  
20           hydroxide, potassium hydroxide, ammonium hydroxide and the like, may be employed to increase pH. The skilled worker would be guided by the nature of the inorganic particulate emulsifying agent. For example, the stability of the emulsion comprising water, ketene dimer and polyaluminum particulate, which is formed by neutralizing polyaluminum chloride with sodium hydroxide, may be affected by pH. Thus, if the emulsion is to be made offsite, the  
25           emulsion should have a pH ranging from about 4.3 to about 4.5. Such an emulsion is stable at least for a period of time (three months or more) from its date of manufacture through storage and transportation up to the date the emulsion is used at a customer's facility, usually a papermaking plant. An emulsion is considered stable, where the emulsion will not substantially separate or stratify during shipment or storage prior to use at the customer's facility.

30           Additionally, other additives may be employed. These additives can include biocides and other

preservatives, which can be added to the emulsion of the present invention in amounts and using techniques known to those in the papermaking industry.

The present invention is useful in commercial papermaking processes.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent.

The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the following examples, all temperatures are set forth uncorrected in degrees Celsius; unless otherwise indicated, all parts and percentages are by weight; and the water is deionized water unless otherwise indicated.

In Examples 1 to 26 and 29, the Brookfield Viscosity is determined using a Brookfield Viscometer, LVF Model with spindle #1 at 60 RPM, available from Brookfield Engineering Laboratories, Inc., Stroughton, MA). In Example 30, the Brookfield Viscosity is determined using a Brookfield Viscometer, LVF Model with spindle #1 at 30 RPM.

## EXAMPLES

### Example 1

Particulate emulsifying agent is prepared by mixing 12.3 parts of Hyper<sup>+</sup> Ion® 1026 (a polyaluminum chloride containing 10.2% Al<sub>2</sub>O<sub>3</sub> and having a percentage basicity of 7-10 and available from General Chemical, Parsippany, NJ), 56.14 parts of deionized water and 19.3 parts of 12% sodium hydroxide aqueous solution to form a particulate. The particulate is sonicated to heat to about 50° to 55°C.

The water phase comprising the polyaluminum particulate and 12.26 parts of melted ketene dimer (Aquapel® 364 dimer) are mixed together, homogenized and cooled to form a starch free and surfactant free emulsion comprising ketene dimer and polyaluminum particulate. The dispersion has a pH in a range of from 4.3 to 4.5 and a total solids content ranging from about 17 to about 18.5 weight percent, a Brookfield Viscosity at 25° C of 5 to 12 centipoise (cps) and a mean particle size of from about 0.3 to about 1.0 micron.

**Example 2**

Particulate emulsifying agent is prepared by mixing 12.3 parts of Hyper<sup>+</sup> Ion® 1026, 45.14 parts of deionized water warmed to a temperature of about 60 to about 70 C, and 19.3 parts of 12% sodium hydroxide aqueous solution to form a warm aqueous phase containing a particulate. 12.26 parts of ketene dimer is melted and added to the warm aqueous phase and is homogenized. The homogenized emulsion is cooled to room temperature and the solids is adjusted by adding about 11 g of water, thereby forming a starch free and surfactant emulsion comprising ketene dimer and particulate. The emulsion has a pH in a range of from 4.3 to 4.5 and a total solids content ranging from about 17 to about 18.5 weight percent, a Brookfield Viscosity at 25° C of 5 to 12 cps and a mean particle size of from about 0.3 to about 1.0 micron.

**Example 3**

33.3 g cationic colloidal silica as a 30% solids solution (Ludox ® CL, available from DuPont Specialty Chemicals, Wilmington, DE) and 66.7 g water are mixed together and heated to 65°C in an oven. 10 g solid alkyl ketene dimer (ketene dimer) (Aquapel ®364, available from Hercules Incorporated, Wilmington, DE) is melted in an oven set at 70°C, and added to aqueous phase. The mix is homogenized using a Cole Parmer ultrasonic Homogenizer (available from Cole Parmer Instrument Company, Vernon Hill, IL) with a one inch solid probe set at 85% amplitude for 4 minutes. The emulsion has a mean particle size of 0.3 microns (using The Malvern Mastersizer available from Malvern Instruments, Inc. Southborough, MA), 25°C Brookfield Viscosity of 4 cps, and pH of 3.55. The emulsion is stable at room temperature for more than 2 years.

**Example 4**

A sample is prepared as in Example 3, except 10 g liquid ketene dimer (Precis ® 787, available from Hercules Incorporated, Wilmington, DE) is used, and the sample is prepared at room temperature. The emulsion has a mean particle size of 0.3 microns, 25°C Brookfield Viscosity of 5 cps, and pH of 3.55.

**Example 5**

A sample is prepared as in Example 4, using 25 g anionic colloidal silica as a 25% solids

solution (Ludox ®HS40 available from DuPont Specialty Chemicals, Wilmington, DE), 75 g water and 10 g liquid ketene dimer (Precis ®787). The emulsion has a mean particle size of 0.27 microns, 25°C Brookfield Viscosity of 5 cps, and pH of 7.97.

5     **Example 6**

A sample is prepared as in Example 3, using 25 g anionic colloidal silica as a 25% solids solution (Ludox® HS40 available from DuPont Specialty Chemicals, Wilmington, DE), 75 g water and 10 g ketene dimer (Aquapel® 364). The emulsion has a mean particle size of 0.92 microns, 25°C Brookfield Viscosity of 4 cps, and pH of 8.70.

10

**Example 7**

A sample is prepared as in Example 3, using 12.5 g colloidal zirconia as a 20% solids solution (Nyacol® Zirconia, available from Nyacol Products Inc, an affiliate of PQ Corporation, Ashland, MA.), 87.5 g water, heated to 65°C with 10 g melted ketene dimer (Aquapel® 364).  
15     The emulsion has a mean particle size of 0.36 microns, 25°C Brookfield Viscosity of 4 cps, pH of 3.74, and is stable for 4 months at ambient temperature.

**Example 8**

A sample is prepared as in Example 3, using 35.7 g colloidal yttria as a 14% solids  
20     solution (Nyacol® Yttria, available from Nyacol Products Inc, an affiliate of PQ Corporation, Ashland, MA.), 64.3 g water, heated to 65°C with 10 g melted ketene dimer (Aquapel® 364). The emulsion has a mean particle size of 0.96 microns, 25°C Brookfield Viscosity of 5 cps, and pH of 6.0.

25     **Example 9**

A sample is prepared as in Example 3, using 25 g colloidal zirconia as a 20% solids solution (Nyacol® Zirconia, available from Nyacol Products Inc, an affiliate of PQ Corporation, Ashland, MA.), 75 g water, and 10 g liquid ketene dimer (Precis ® 787). The emulsion has a mean particle size of 0.39 microns, 25°C Brookfield Viscosity of 5 cps, pH of 3.80.

30



**Example 10**

6.15 g of a 20% solids ferric chloride solution and 76.76 g of water are mixed together, 4.83 g of a 12% solids solution of sodium hydroxide is added with vigorous stirring to form a particulate. The solution has a pH of 2.44. The solution is sonicated, using a Cole Parmer  
5 Ultrasonic Homogenizer with a one inch solid probe set at 85% amplitude, 4 minutes to heat above 50°C. 12.26 g melted ketene dimer (Aquapel ®364) is added and the mixture is sonicated a further 4 minutes to make the emulsion. The resultant emulsion has a mean particle size of 2.19 microns, and pH of 1.97.

**Example 11**

A sample is prepared as in Example 10 using 12.3 g Gen + Ion ® 7026 (polyaluminum hydroxychloride with 5.4% Al and 7-10% Basicity, available from General Chemicals, Syracuse NY.), 56.14 g water, 19.3 g of 12% sodium hydroxide solution and 12.26 g ketene dimer (Aquapel ®364). The resultant emulsion has a mean particle size of 0.56 microns,  
15 pH of 4.31 and 25°C Brookfield Viscosity of 5 cps. Accelerated emulsion stability shows that this emulsion has through 4 weeks at 25°C a 2.2% stratification (as measured from the determination of solids at the bottom of the jar (150°C for 30 minutes in an oven) vs. the starting total solids).

**Example 12**

A sample is prepared as in Example 10 using 28.14 Gen + Pac ® 4370 (polyaluminum hydroxychloride with 12.3% Al and 70-75% Basicity, available from General Chemicals, Syracuse NY.), 58.36 g water, 13.5 g of 12% sodium hydroxide solution and 10 g alkenyl succinic anhydride (ASA) (Bersize ®6938, available from Bercen, Inc. a division of  
25 Cranston Print Works Company, Cranston, RI.). The resultant emulsion has a mean particle size of 1.9 microns, pH of 4.12 and 25°C Brookfield Viscosity of 6 cps.

**Example 13**

A sample is prepared as in Example 10 using 24 g Gen + Ion ® 7026 (polyaluminum  
30 hydroxychloride with 5.4% Al and 7-10% basicity, available from General Chemicals, Syracuse

NY.), 59.55 g water, 16.45 g of 15% ammonium hydroxide solution and 10 g ketene dimer (Aquapel ®364). The resultant emulsion has a mean particle size of 0.27 microns, pH of 3.95 and 25°C Brookfield Viscosity of 4 cps.

5     **Example 14**

A sample is prepared as in Example 10 using 10 g of 50% aluminum sulfate solution (alum) (available from General Chemical Corporation, Parsippany, NJ) 51.5 g water, 38.5 g of 3% sodium hydroxide solution and 10 g ketene dimer (Aquapel ®364). The resultant emulsion has a mean particle size of 9.46 microns, and pH of 4.11.

10

**Example 15**

A sample is prepared as in Example 10 using 30 g of 50% alum solution, 41.11 g water, 28.89 g of 12% sodium hydroxide solution and 10 g alkenyl succinic acid anhydride(ASA-150 available from Dixie Chemical Company, Inc. Houston, TX). The resultant emulsion has a mean particle size of 6.09 microns, 25°C Brookfield Viscosity of 18 cps, and pH of 4.30.

15

**Example 16**

A sample is prepared as in Example 15 using 10 g liquid ketene dimer (Precis ® 787). The resultant emulsion has a mean particle size of 6.60 microns, 25°C Brookfield Viscosity of 58 cps, and pH of 4.30.

20

**Example 17**

A sample is prepared as in Example 10 using 20 g WT195 (polyaluminum chloride and zirconyl chloride, obtained from Summit Research Labs – Huguenot Division, Huguenot, NY.), 75.96 g water, 4.04 g of 12% sodium hydroxide solution and 10 g ketene dimer (Aquapel ®364). The resultant emulsion has a mean particle size of 0.44 microns, and pH of 4.61.

25

**Example 18**

A sample is prepared as in Example 10 using 12.8 g Gen<sup>+</sup> Ion ® 7026 (PAC), 1.25 g 50% alum solution, 68.95 g water, 17 g of 12% sodium hydroxide solution and 10 g ketene dimer

30

(Aquapel ®364). The resultant emulsion has a mean particle size of 26.2 microns, pH of 3.28 and 25°C Brookfield Viscosity of 68 cps.

#### Example 19

5           A sample is prepared as in Example 10 using 20.40 g Gen + Pac ® 4370 (PAC), 24.14 g 25% alum solution, 41.96 g water, 13.5 g of 12% sodium hydroxide solution and 10 g ASA-150. The resultant emulsion has a mean particle size of 6.65 microns and pH of 2.92.

#### Example 20

10           0.3 g fumed silica (0.007 microns, (available from Aldrich Chemical Company, Milwaukee, WI.) is mixed with 90 g of 0.00002 molar aqueous solution of cetyltrimethylammonium bromide (available from Aldrich Chemical Company, Milwaukee, WI.) The mixture is then stirred for one hour, and is sonicated four minutes as in Example 8. 10 g melted ketene dimer (Aquapel ®364) is added and the mixture is sonicated a further 4  
15 minutes. An emulsion with mean particle size of 0.24 microns, and pH of 3.33 is prepared.

#### Example 21

          0.3 g Aerosil ® R805 (hydrophobically modified silica available from Degussa Corporation, Silica Division, Ridgefield Park, NJ) is mixed with 10 g liquid ketene dimer  
20 (Precis ® 787). 100 g of water is added and the mixture is sonicated for 4 minutes as in Example 10. An emulsion with mean particle size of 0.41 microns, and pH of 3.01 is prepared.

#### Example 22

25           0.3 g Aerosil ® R202 (hydrophobically modified silica available from Degussa Corporation, Silica Division, Ridgefield Park, NJ) is mixed with 10 g ketene dimer (Aquapel ®364) and is allowed to melt in an oven at 70°C. 100 g of 65°C water is added and the mixture is sonicated for 4 minutes as in Example 10. An emulsion is prepared.

30

**Example 23**

To 15 g cationic colloidal silica at 30% solids (Ludox ® CL) 75 g of 1.46% sulfuric acid solution is added with stirring to a very slight haze, 10 g of 50% alum solution is then added drop wise with stirring producing a clear solution. The solution is sonicated 4 minutes as in Example 10 and 10 g melted ketene dimer (Aquapel ®364) is added. The mixture is sonicated a further 4 minutes. An emulsion with mean particle size of 2.23 microns, 25°C Brookfield Viscosity of 6 cps and pH of 2.87 is prepared.

**Example 24**

To 12.5 g anionic colloidal silica at 25% solids (Ludox ® HS40) 77.5 g of water is added, 10 g of 50% alum solution is then added drop wise with stirring producing a gel like particulate. The solution is sonicated 4 minutes as in Example 8 and 10 g melted ketene dimer (Aquapel ®364). The mixture is sonicated a further 4 minutes. An emulsion with mean particle size of 1.54 microns, 25°C Brookfield Viscosity of 43 cps and pH of 3.11 is prepared.

**Example 25**

A sample is prepared as in Example 4, except using 10 g ASA-150. An emulsion with mean particle size of 0.56 microns and pH of 3.44 is prepared.

**Example 26**

A sample is prepared as in Example 10 using 52.9 g of 30.6% solution aluminum nitrate nonahydrate (available from Aldrich Chemical Company, Milwaukee, WI.) and 60.54 g of 33.3% solution of sodium phosphate monobasic (available from J. T. Baker a division of Mallinckrodt Baker, Inc. Phillipsburg, NJ.), the pH is adjusted to 2.2 by adding, with stirring, 10.75 g of 12% sodium hydroxide solution. The mixture is sonicated 5 minutes, 10 g melted ketene dimer (Aquapel ®364) is added and the blend is sonicated a further 2 minutes. An emulsion with mean particle size of 44.89 microns, 25°C Brookfield Viscosity of 25 cps and pH of 2.18 is prepared.

**Example 27**

Following TAPPI Method T227 the Canadian Standard Freeness (CSF) test for drainage on Example 11 shows improved drainage with a CSF of 551 vs. 496 for a Hercon ®115 (available from Hercules Incorporated, Wilmington, DE.) control sample, an improvement of 11%.

The CSF test is conducted on a pulp blend of 30/70 bleached softwood/hardwood kraft containing 20% PCC (precipitated calcium carbonate) filler (Albacar 5970, available from Pfizer Inc., New York, NY) prepared at 0.323% solids in standard hard water. An aliquot of 827 g of the pulp is poured into a beaker and is stirred with an over head stirrer; 0.4 mls (12 lbs per ton) of 3% Stalok 400 starch solution (Stalok 400 available from A.S. Stanley manufacturing Co., Decatur, IL.) is added and is stirred for one minute. 0.8 mls of 0.5% active solids solution (based on dimer content) of sizing agent (4 lbs per ton) is added and is stirred one minute. The beaker is removed from the overhead stirrer; 0.16 ml of 2.5% solids solution of Ludox® SM (available from DuPont Specialty Chemicals, Wilmington, Del) is added and is stirred gently with a spatula for one second. The contents of the beaker is poured into a one liter graduated cylinder and is made up to 1000 mls with standard hard water.

The CSF test is conducted by using a Schopper-Riegler Freeness Tester and the data obtained is converted to CSF.

**Example 28**

A paper product which is surface sized from the emulsion described in Example 19 using the Western Michigan University Pilot Paper Machine, as described in United States Patent 6,048,392, has HST sizing (measured by the Hercules Sizing Tester using #2 Ink) of 93 seconds and maintained sizing in the size press for the duration of the 40 minute test. U.S. Patent No. 6,048,392 describes the experimental set up. A conventionally prepared ASA emulsion comprising surfactant and starch does not work in the size press whereas an ASA emulsion made in accordance with the present invention maintains its sizing through the 40 minute duration of the test.

**Example 29**

A sample is prepared as in Example 10 using 50 g of a 1% sodium oleate solution (available from Aldrich Chemical Company, Milwaukee, WI.), 36 g water, 14 g 1% alum solution and 10 g ASA-150. The sample is sonicated 10 minutes to form the emulsion. An emulsion with mean particle size of 1.41 microns, 25°C Brookfield Viscosity of 4 cps and pH of 4.10 is prepared.

**Example 30**

A sample is prepared by weighing 902.8 g tap water at 30°C into a stainless steel beaker and heating to 55°C on a hot plate with an overhead stirrer. 256.0 g Gen@Ion 7026 (available from General Chemical) is added and with continued stirring 386 g of 12% sodium hydroxide solution is added slowly to form the particulate. 245.2 g Aquapel ® 364 is added and is allowed to melt. The mixture is passed through a microfluidizer (model number HC-5000 Sanitary Pneumatic Homogenizer, available from Microfluidics International Corporation, Newton, MA) at 3400 psi 5 times. An emulsion at 20.28% total solids is prepared. 1461.44 g of the emulsion is reduced to 17.8% solids with 180.64 g tap water. The final adjusted emulsion has a mean particle size of 3.07 microns, total solids of 17.9%, 25° C Brookfield Viscosity of 305 cps.

**Example 31**

A sample is prepared by weighing 1122.8 g water into a 2 liter stainless steel beaker with an overhead stirrer. 246.0 g Gen@Ion 7026 is added and with continued stirring 386 g of 12% sodium hydroxide solution is added slowly to form the particulate. The mixture is passed through a microfluidizer model number HC-5000 at 3400 psi. 1316.1 g of this mixture is weighed into a 2 liter stainless steel beaker and is heated to 55°C on at hot plate with stirring. 183.9 g Aquapel ® 364 is added and is allowed to melt. The mixture is passed through a microfluidizer model number HC-5000 at 3400 psi 3 times to prepare the emulsion. An emulsion with a mean particle size of 2.11 microns, total solids of 17.6%, 25° C Brookfield Viscosity of 17 cps and pH of 4.54 is prepared.

It is noted that the foregoing examples have been provided merely for the purpose of

explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to an exemplary embodiment, it is understood that the words which have been used herein are words of description and illustration, rather than words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.

## WHAT IS CLAIMED IS:

1. A method of preparing an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the sizing agent, the method comprising:

5        admixing water, the inorganic particulate emulsifying agent and the sizing agent to form the aqueous emulsion.

2. The method of claim 1 wherein the inorganic particulate emulsifying agent is selected from clay, silica, zeolite, mica, calcium carbonate, calcium phosphate, calcium sulfate, aluminum oxide, aluminum hydroxide, aluminum phosphate, aluminum silicate,  
10        magnesium phosphate, magnesium silicate, polyaluminum chloride, polyaluminum phosphate, polyaluminum silicate, ferrous phosphate, ferrous silicate, ferrous oxide, ferric phosphate, ferric silicate, ferric oxide, yttria, zirconia, or mixtures thereof.

3. The method of claim 1 wherein the inorganic particulate emulsifying agent is selected from at least substantially water insoluble compounds of metals selected from  
15        aluminum, barium, calcium, cerium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, strontium, titanium, zinc, zirconium, or mixtures thereof.

4. The method of claim 1 wherein the inorganic particulate emulsifying agent is selected from colloidal silica, colloidal alumina or colloidal zirconia.

5. The method of claim 1 wherein the aqueous emulsion comprises globules of the  
20        sizing agent emulsified with the inorganic particulate emulsifying agent and having a particle size of about 0.1 to about 100 microns.

6. The method of claim 5 wherein the globules of the sizing agent have a particle size of about 0.1 to about 20 microns.

7. The method of claim 6 wherein the globules of the sizing agent have a particle size  
25        of about 0.1 to about 2 microns.

8. The method of claim 6 wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

9. The method of claim 1 wherein a first water soluble salt is added to the water to form a solution comprising the first water soluble salt and adding a second water soluble salt  
30        to the solution to form a particulate comprising the inorganic particulate emulsifying agent.



10. The method of claim 1 wherein the sizing agent is selected from 2-oxetanone dimer or multimer, alkenyl succinic anhydride, rosin or carbamoyl chloride.

11. The method of claim 10 wherein polyaluminum chloride is added to the water to form a solution comprising the polyaluminum chloride and alkali is added to the solution to form the inorganic particulate emulsifying agent comprising polyaluminum particulate.

12. The method of claim 11 wherein the aqueous emulsion is sonicated or homogenized.

13. The method of claim 10 wherein the pH of the aqueous emulsion is from about 4.3 to about 4.5.

14. The method of claim 13 wherein the sizing agent is 2-oxetanone,3(C12-C16)alkyl,4-(C13-C17)alkylidene and the inorganic particulate emulsifying agent is polyaluminum particulate.

15. The method of claim 1 wherein the inorganic particulate emulsifying agent is present in an amount from about 0.1 to about 100 percent by weight, based on the weight of the sizing agent.

16. The method of claim 15 wherein the inorganic particulate emulsifying agent is present in an amount from about 10 to about 25 percent by weight, based on the weight of the sizing agent.

17. The method of claim 1 wherein the sizing agent is solid at room temperature and further comprising heating the sizing agent to melt the sizing agent, heating the water to a temperature to at least about a melting point of the sizing agent, and admixing the melted sizing agent, the heated water and the inorganic particulate emulsifying agent to form the aqueous emulsion.

18. The method of claim 1 where the sizing agent is solid at room temperature and the water is heated to a temperature sufficient to melt the sizing agent.

19. The method of claim 1 wherein the sizing agent is solid at room temperature, and further comprising dissolving the sizing agent in an organic solvent, admixing the water, the sizing agent dissolved in the organic solvent and the inorganic particulate emulsifying agent to form the aqueous emulsion and stripping the organic solvent from the emulsion.

20. The method of claim 1 wherein the sizing agent is carbamoyl chloride and

wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

21. The method of claim 1 wherein the sizing agent is rosin and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

22. The method of claim 1 wherein the sizing agent is 2-oxetanone dimer or  
5 multimer and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

23. The method of claim 22 further comprising adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine.

24. The method of claim 22 further comprising surface sizing paper with the aqueous  
10 emulsion.

25. The method of claim 1 wherein the sizing agent is alkenyl succinic anhydride and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

26. The method of claim 25 further comprising adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine.

27. The method of claim 25 further comprising surface sizing paper with the aqueous  
15 emulsion.

28. A method of preparing an aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent comprising polyaluminum particulate, wherein the sizing agent is selected from one or more of 2-oxetanone,3-(C12-C16)alkyl,4-(C13-  
20 C17)alkylidene, 2-oxetenone,3-(C14-C16)alkyl,4-(C15-C17)alkylidene or 2-oxetanone,3-eicosyl,4-heneicosylidene, the method comprising:

dissolving polyaluminum salt selected from one or more of polyaluminum chloride, polyaluminum hydroxychloride or polyaluminum chloride containing sulfate in water to form a solution,

25 adding to the solution an amount of alkali sufficient to form a polyaluminum particulate,

heating the water up to a melting temperature of the sizing agent,

admixing the sizing agent with the heated water containing the polyaluminum particulate, and

30 sonificating or homogenizing the admixed water to form the aqueous emulsion.

29. The method of claim 28 wherein the sizing agent is melted prior to its addition to the water.

30. The method of claim 29 further comprising adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine.

5        31. The method of claim 29 further comprising surface sizing paper with the aqueous emulsion.

32. A method of preparing an aqueous emulsion comprising water, alkenyl succinic anhydride and inorganic particulate emulsifying agent comprising polyaluminum particulate, the method comprising:

10        dissolving polyaluminum salt selected from one or more of polyaluminum chloride, polyaluminum hydroxychloride or polyaluminum chloride containing sulfate in water to form a solution,

adding to the solution an amount of alkali sufficient to form a polyaluminum particulate,

15        admixing the alkenyl succinic anhydride with the water containing the polyaluminum particulate, and

sonificating or homogenizing the admixed water to form the aqueous emulsion.

33. The method of claim 32 further comprising adding the aqueous emulsion to a pulp slurry in a headbox of a papermaking machine.

20        34. The method of claim 32 further comprising surface sizing a paper with the aqueous emulsion.

35. An aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the sizing agent.

25        36. The aqueous emulsion of claim 35 wherein the inorganic particulate emulsifying agent is selected from clay, silica, zeolite, mica, calcium carbonate, calcium phosphate, calcium sulfate, aluminum oxide, aluminum hydroxide, aluminum phosphate, aluminum silicate, magnesium phosphate, magnesium silicate, polyaluminum chlorohydroxide, polyaluminum phosphate, polyaluminum silicate, ferrous phosphate, ferrous silicate, ferrous oxide, ferric phosphate, ferric silicate, ferric oxide yttria, or mixtures thereof.

30        37. The aqueous emulsion of claim 35 wherein the inorganic particulate emulsifying

agent is selected from at least substantially water insoluble compounds of metals selected from aluminum, barium, calcium, cerium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, strontium, titanium, zinc, zirconium, or mixtures thereof.

38. The aqueous emulsion of claim 35 wherein the inorganic particulate emulsifying agent is selected from colloidal silica, colloidal alumina or colloidal zirconia.

39. The aqueous emulsion of claim 35 wherein the aqueous emulsion comprises globules of the sizing agent emulsified with the inorganic particulate emulsifying agent and having a particle size of about 0.1 to about 100 microns.

40. The aqueous emulsion of claim 39 wherein the globules of the sizing agent have a particle size of about 0.1 to about 20 microns.

41. The aqueous emulsion of claim 40 wherein the globules of the sizing agent have a particle size of about 0.1 to about 2 microns.

42. The aqueous emulsion of claim 41 wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

43. The aqueous emulsion of claim 35 wherein the sizing agent is selected from carbamoyl chloride, rosin, 2-oxetanone dimer or multimer, or alkenyl succinic anhydride.

44. The aqueous emulsion of claim 43 wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

45. The aqueous emulsion of claim 44 wherein the sizing agent is 2-oxetanone,3-(C12-C16)alkyl,4-(C13-C17)alkylidene and the pH of the aqueous emulsion ranges from about 4.3 to about 4.5.

46. The aqueous emulsion of claim 35 wherein the inorganic particulate emulsifying agent is present in an amount from about 5 to about 35 percent by weight, based on the weight of the sizing agent.

47. The aqueous emulsion of claim 46 wherein the inorganic particulate emulsifying agent is present in an amount from about 10 to about 25 percent by weight, based on the weight of the sizing agent.

48. The aqueous emulsion of claim 35 wherein the sizing agent is carbamoyl chloride and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

49. The aqueous emulsion of claim 35 wherein the sizing agent is rosin and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

50. The aqueous emulsion of claim 35 wherein the sizing agent is 2-oxetanone dimer or multimer and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

51. The aqueous emulsion of claim 35 wherein the sizing agent is alkenyl succinic anhydride and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

52. A method of processing cellulosic pulp comprising adding to the cellulosic pulp, in a wet part of a papermaking process, the emulsion of claim 35.

53. A method of sizing paper comprising surface sizing paper with the emulsion of claim 35.

54. An aqueous emulsion comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming the emulsion between the sizing agent and water, wherein the sizing agent is selected from one or more of 2-oxetanone,3-(C12-C16)alkyl,4-(C13-C17)alkylidene, 2-oxetenone,3-(C14-C16)alkyl,4-(C15-C17)alkylidene or 2-oxetanone,3-eicosyl,4-heneicosylidene, and wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

55. A method of processing cellulosic pulp comprising adding to the cellulosic pulp, in a wet part of a papermaking process, the emulsion of claim 54.

56. A method of sizing paper comprising surface sizing paper with the emulsion of claim 54.

57. An aqueous emulsion comprising water, alkenyl succinic anhydride and inorganic particulate emulsifying agent capable of forming the emulsion between the water and the alkenyl succinic anhydride, wherein the inorganic particulate emulsifying agent comprises polyaluminum particulate.

58. A method of processing cellulosic pulp comprising adding to the cellulosic pulp, in a wet part of a papermaking process, the emulsion of claim 57.

59. A method of sizing paper comprising surface sizing paper with the emulsion of claim 58.

60. A paper product made with the emulsion of claim 35.
61. A cardboard product made with the emulsion of claim 35.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
31 January 2002 (31.01.2002)

PCT

(10) International Publication Number  
**WO 02/08514 A3**

(51) International Patent Classification<sup>7</sup>: **D21H 21/16**,  
17/67, 17/74

(21) International Application Number: **PCT/US01/21809**

(22) International Filing Date: **9 July 2001 (09.07.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
**09/626,160** **26 July 2000 (26.07.2000)** **US**

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant: **HERCULES INCORPORATED [US/US];**  
Hercules Plaza, 1313 N. Market Street, Wilmington, DE  
19894-0001 (US).

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(72) Inventors: **NEWPORT, John, F., L.;** 239 Pond View Drive, Chadds Ford, PA 19317 (US). **WEATHERDON, Jennifer;** 25 Hawthorne Avenue, Newark, DE 19711 (US).

(88) Date of publication of the international search report:  
**25 April 2002**

(74) Agent: **ROSSI, Joanne, Mary, Fobare;** Hercules Incorporated, Hercules Plaza, 1313 N. Market Street, Wilmington, DE 19894-0001 (US).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 02/08514 A3**

(54) Title: **METHOD OF MAKING SIZING EMULSION AND SIZING EMULSION**

(57) Abstract: The present invention relates to methods for preparing emulsions comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming an emulsion between the water and an oil phase comprising the sizing agent, and to emulsions comprising water, sizing agent and inorganic particulate emulsifying agent capable of forming an emulsion between the water and an oil phase comprising the sizing agent.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/21809

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21H21/16 D21H17/67 D21H17/74

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 800 750 A (PATENT AND LICENSING CORP) 3 September 1958 (1958-09-03) the whole document ---	1,2,35, 36,60,61
X	WO 97 31152 A (ALLIED COLLOIDS LTD ; PEUTHERER PETER (GB); WARING IAN MARK (GB); C) 28 August 1997 (1997-08-28)  page 7, line 1 - line 33 examples ---	1,2,10, 35,36, 52,53, 60,61
P,X	EP 1 099 795 A (AKZO NOBEL NV) 16 May 2001 (2001-05-16)  the whole document ---	1,4-8, 10,25, 26,35, 38-44, 51,52, 57-61



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

11 February 2002

Date of mailing of the international search report

22/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Songy, 0



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/21809

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 564 994 A (HERCULES INC)</p> <p>13 October 1993 (1993-10-13)</p> <p>-----</p>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/21809

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 800750	A	03-09-1958	FR 1175836 A	02-04-1959
WO 9731152	A	28-08-1997	AU 715436 B2	03-02-2000
			AU 1887797 A	10-09-1997
			BR 9707734 A	27-07-1999
			CA 2247211 A1	28-08-1997
			CN 1214093 A	14-04-1999
			CZ 9802580 A3	17-03-1999
			EP 0882156 A1	09-12-1998
			WO 9731152 A1	28-08-1997
			HU 9900794 A2	28-07-1999
			JP 2000506227 T	23-05-2000
			NO 983857 A	21-10-1998
			PL 328615 A1	01-02-1999
			RU 2150542 C1	10-06-2000
			SK 115898 A3	11-06-1999
			TW 383345 B	01-03-2000
			US 6284099 B1	04-09-2001
			ZA 9701570 A	24-02-1998
EP 1099795	A	16-05-2001	EP 1099795 A1	16-05-2001
			AU 6032800 A	31-01-2001
			WO 0100927 A1	04-01-2001
EP 0564994	A	13-10-1993	BR 9301446 A	13-10-1993
			CA 2092955 A1	07-10-1993
			DE 69303649 D1	22-08-1996
			DE 69303649 T2	20-02-1997
			EP 0564994 A1	13-10-1993
			JP 6299495 A	25-10-1994
			KR 238837 B1	15-01-2000
			US 5433776 A	18-07-1995